

Fourth Annual Conference on Carbon Capture & Sequestration

*Developing Potential Paths Forward Based on the
Knowledge, Science and Experience to Date*

Geologic - Frio Brine Field Project (1)

Geochemistry of Water and Gases in the Frio Brine Pilot Test: Baseline Data and Changes During and Post CO₂ Injection

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Topics Discussed

- Chemical and isotopic compositions of water and gases in the Frio– Baseline, during and post injection results.
- How are such data obtained and why are they important to CO₂ sequestration?
- Water-mineral-CO₂ interactions in the Frio.
- Environmental implications of post injection results– Leakage of CO₂ and brine.
- Future plans and concluding remarks.



Why Detailed Chemical Data?

- Investigate most sensitive chemical signals to track the injected CO₂ and to understand its transport in the reservoir and through cap rocks and seals.
- Investigate inorganic and organic species mobilized by interaction of injected CO₂ and reservoir rock.
- Chemical data required for short term and long term geochemical simulations needed to predict CO₂-brine-mineral interactions that impact reservoir capacity and injectivity.
- Required to evaluate environmental impacts resulting from leakage of CO₂ and brine.

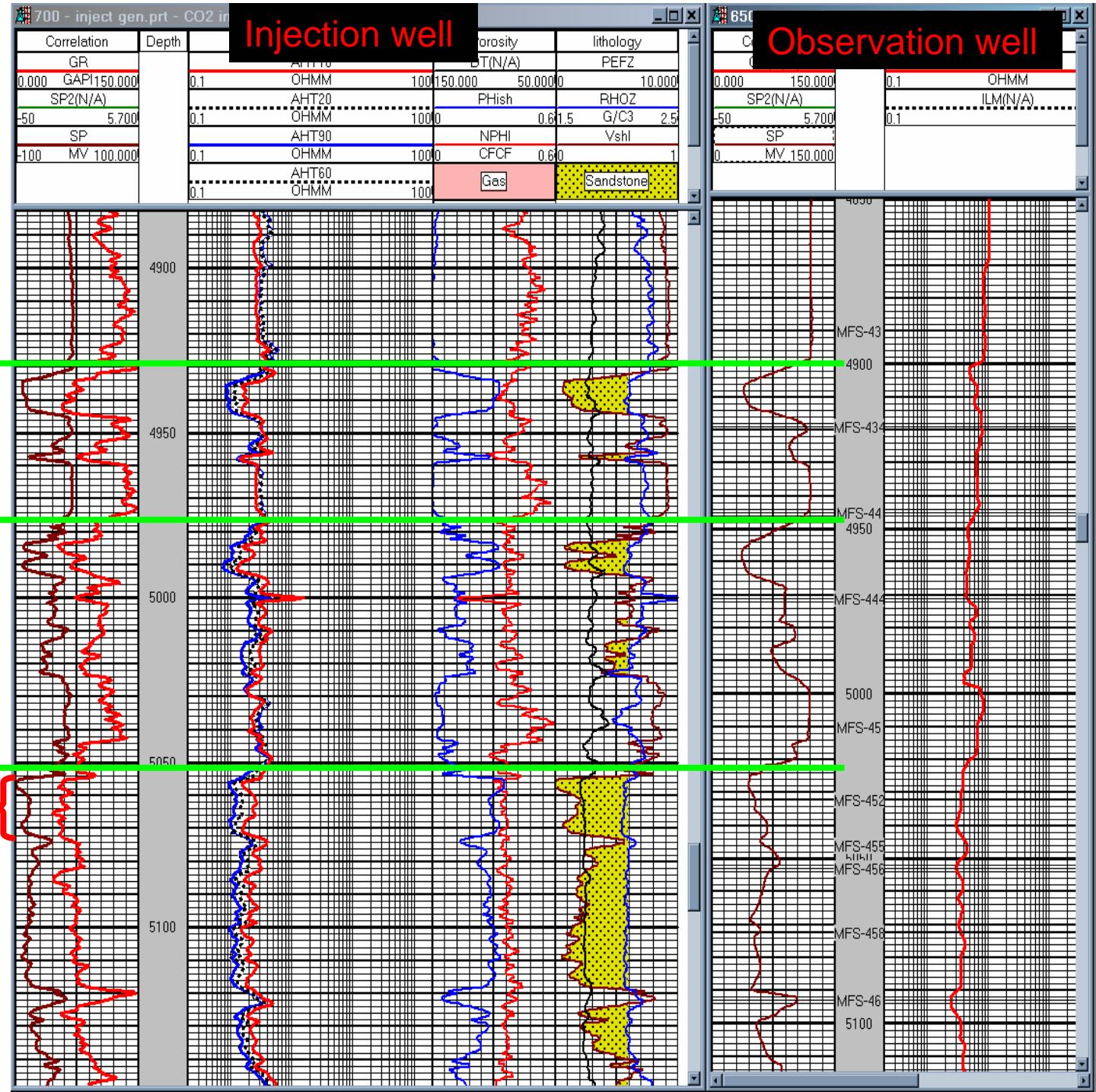
Open Hole logs

Top A ss

Top B ss

Top C ss
Proposed
injection zone

Hovorka et al.,
2004



Chemical Data on Formation Waters in Sedimentary Basins

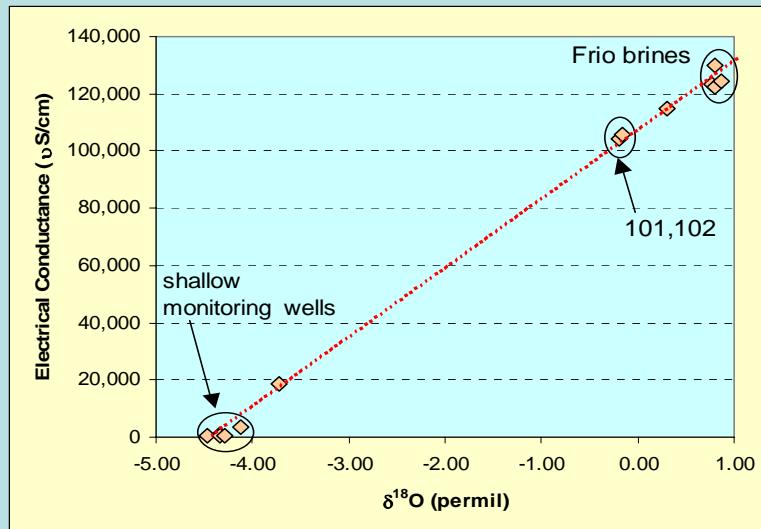
Sources and reliability:

- 1- SP and other geophysical logs– Frio = 125,000 mg/L TDS
 - 2- Drill stem tests and other tools, e.g. MDT—72,000 mg/L
 - 3- Database from petroleum co. and other sources– Liberty County
Frio = 30,000, 65,000
Yegua ~ 115,000
 - 4- Frio sampling = 93,000 mg/L

A national produced-water geochemistry database

Otton, Breit, Kharaka and Rice, at:

<http://energy.cr.usgs.gov/prov/prodwat/intro.htm>



Frio CO₂ Field sampling

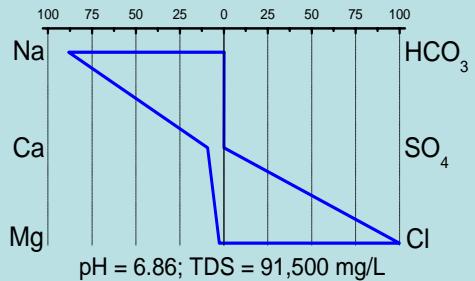
Drilling & test water tagged with dye tracers

Date	Site	Sampling info	Sample series
June 3, 2004	injection well	MDT tool	04FCO ₂ -100
Jul 23-Aug 2, 2004	injection well, monitoring well & gw wells	surface sampling (N ₂), Kuster, submers.pump	04FCO ₂ -200
Oct 4-7, 2004	monitoring well	U-tube	04FCO ₂ -300
Oct 29-Nov 3, 2004	monitoring well	U-tube	04FCO ₂ -400
April 4-6, 2005	injection well & monitoring well	surface sampling (N ₂) & Kuster	05FCO ₂ -100

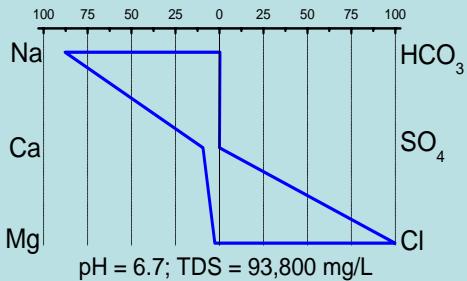


Salinity and normalized conc. of major cations and anions

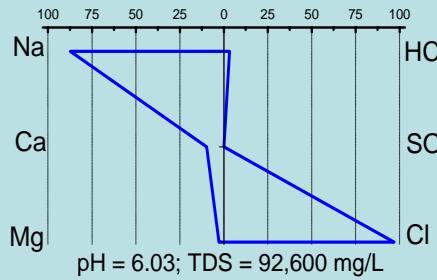
04-FCO2-208 (injection well)



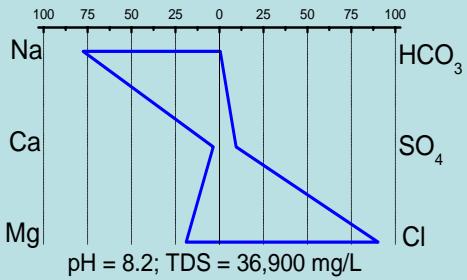
04FCO2-218 (monitoring well, C-sand)



04FCO2-337 (monitoring well; post injection)

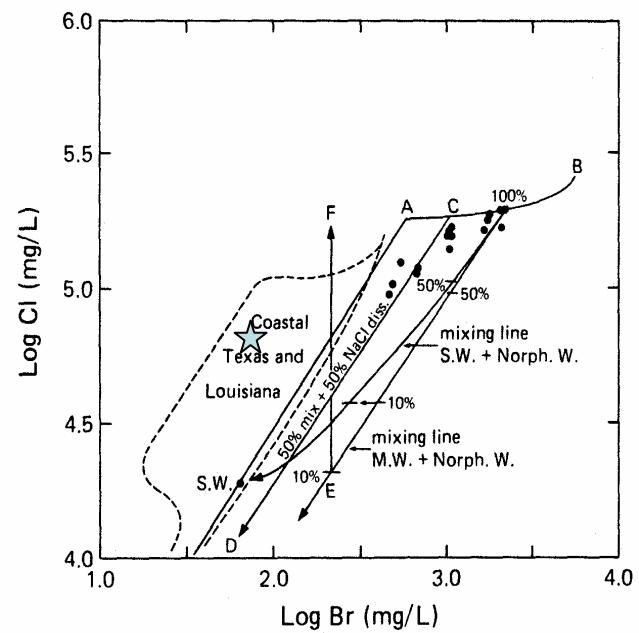


seawater

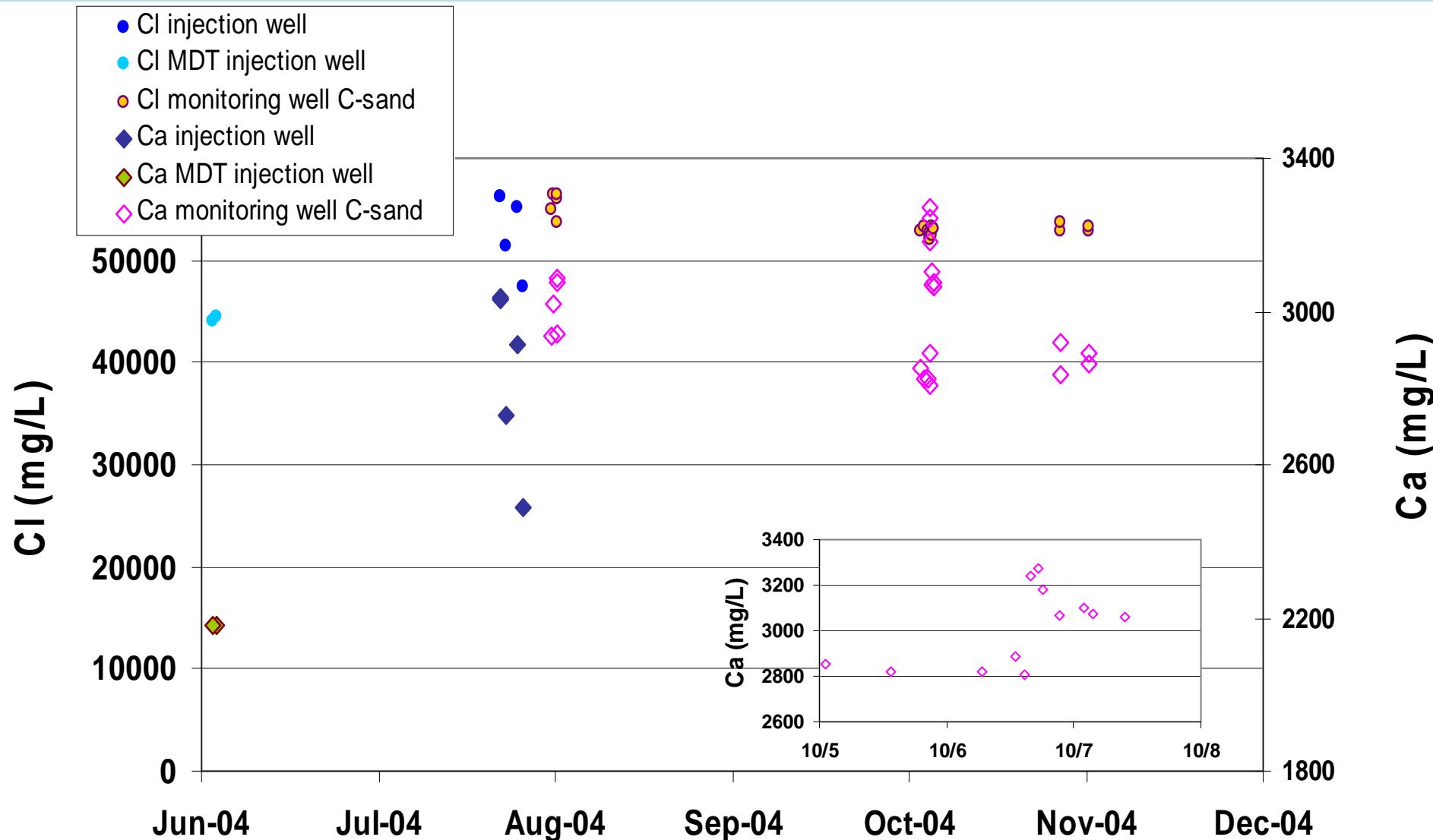


[milliequivalents/liter, normalized to 100%]

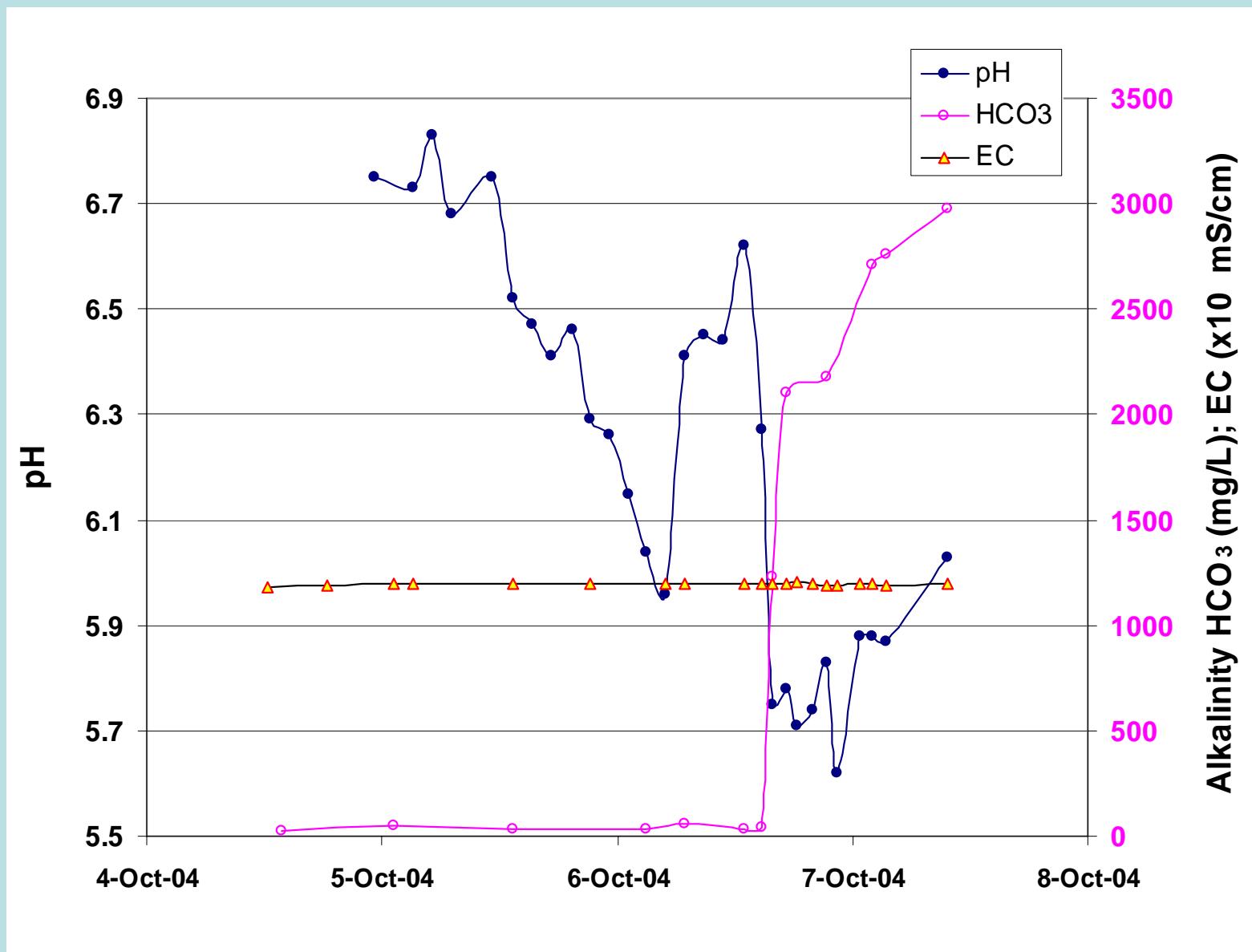
Br-Cl indicate origin of solutes
(* Frio value)
Kharaka & Hanor, 2004



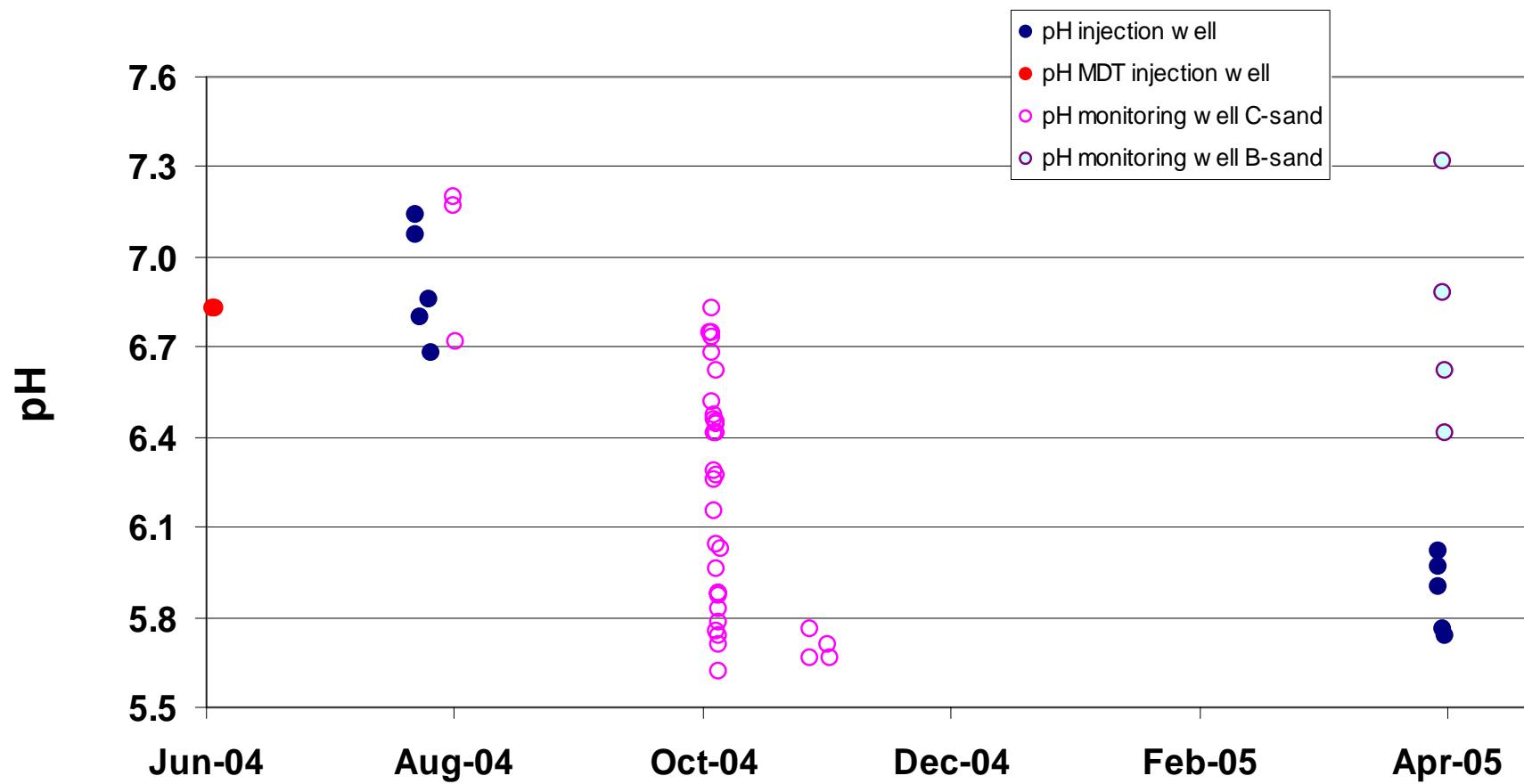
Frio Cl & Ca (6/04-11/04)



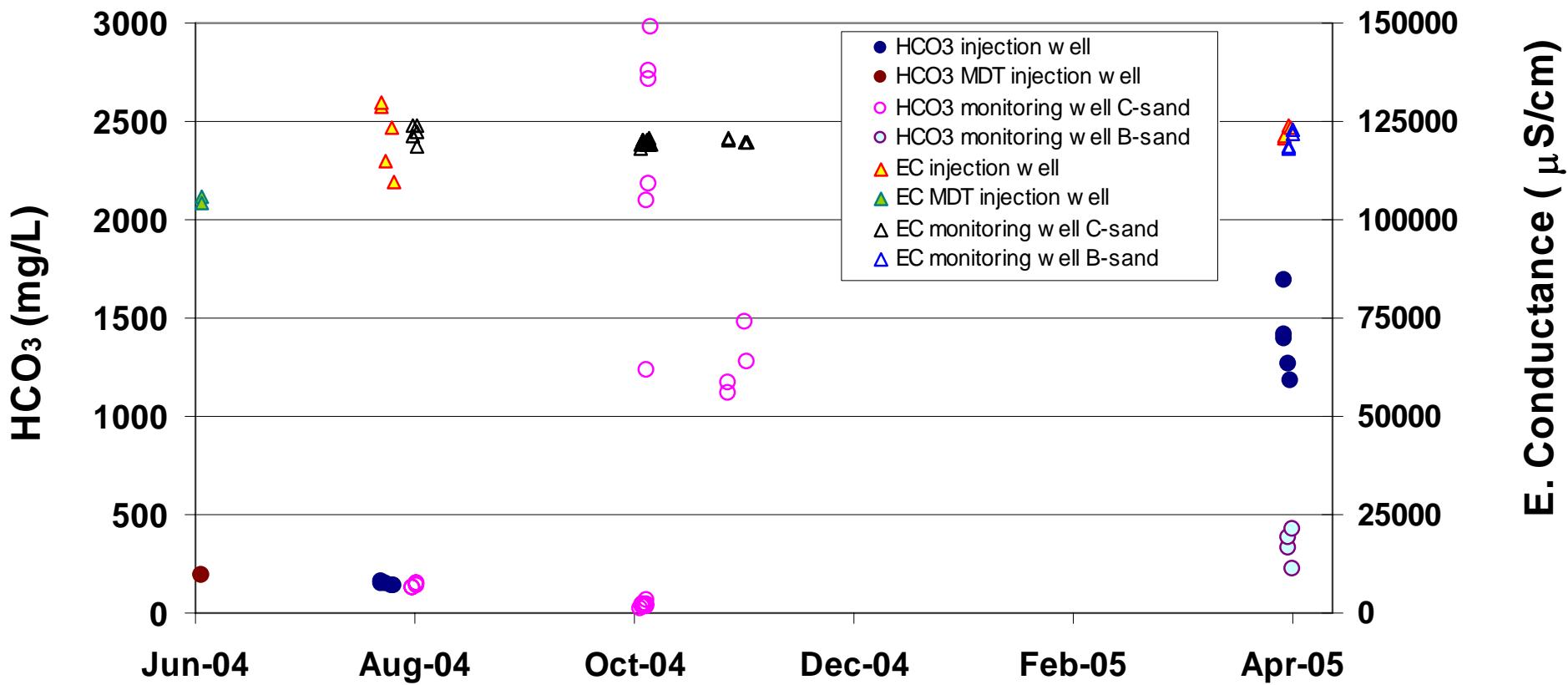
Selected chemical data from monitoring well during CO₂ injection



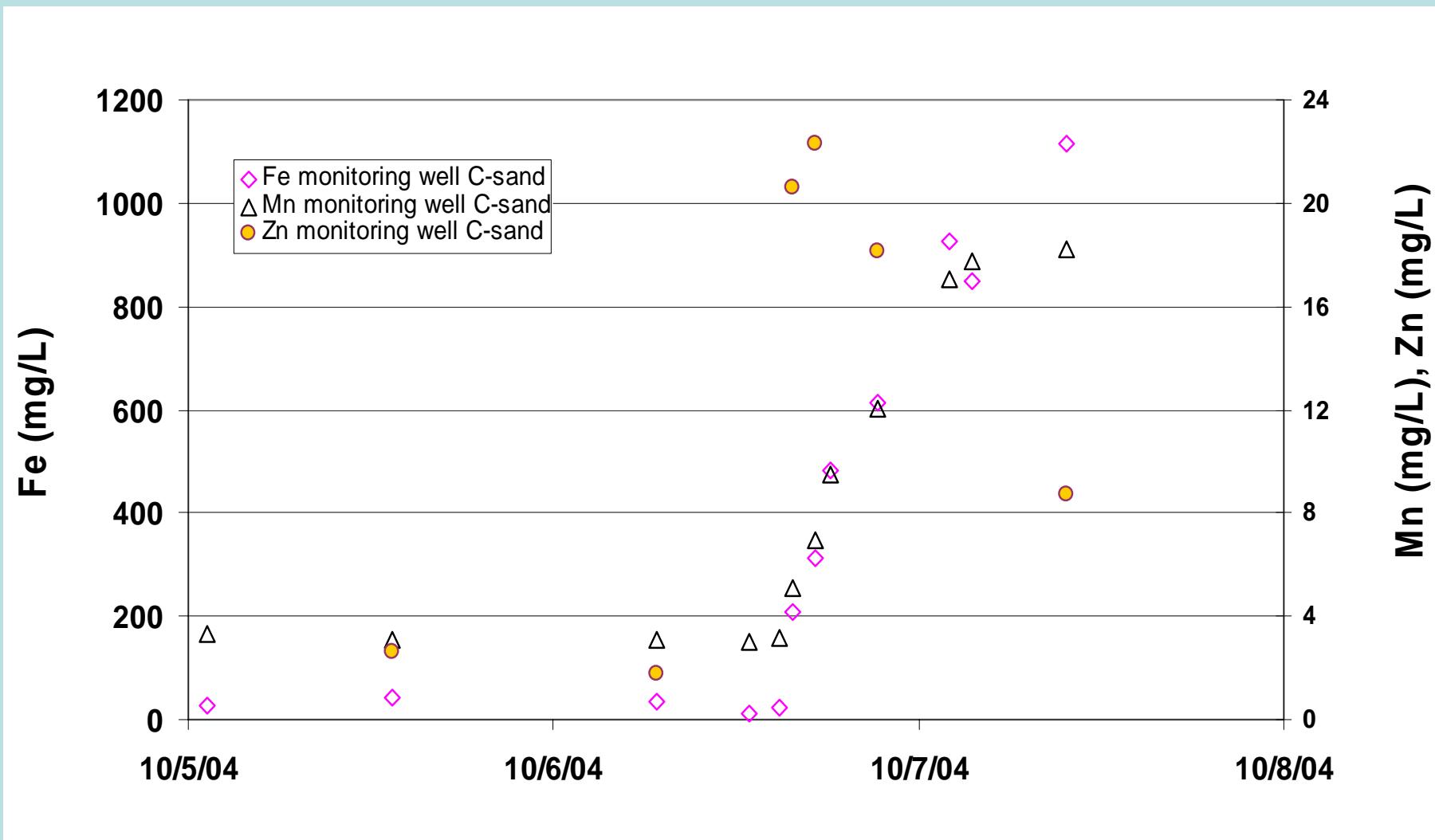
pH values of Frio brine for 6/04-4/05



HCO₃ and conductance of Frio samples (6/04-4/05)

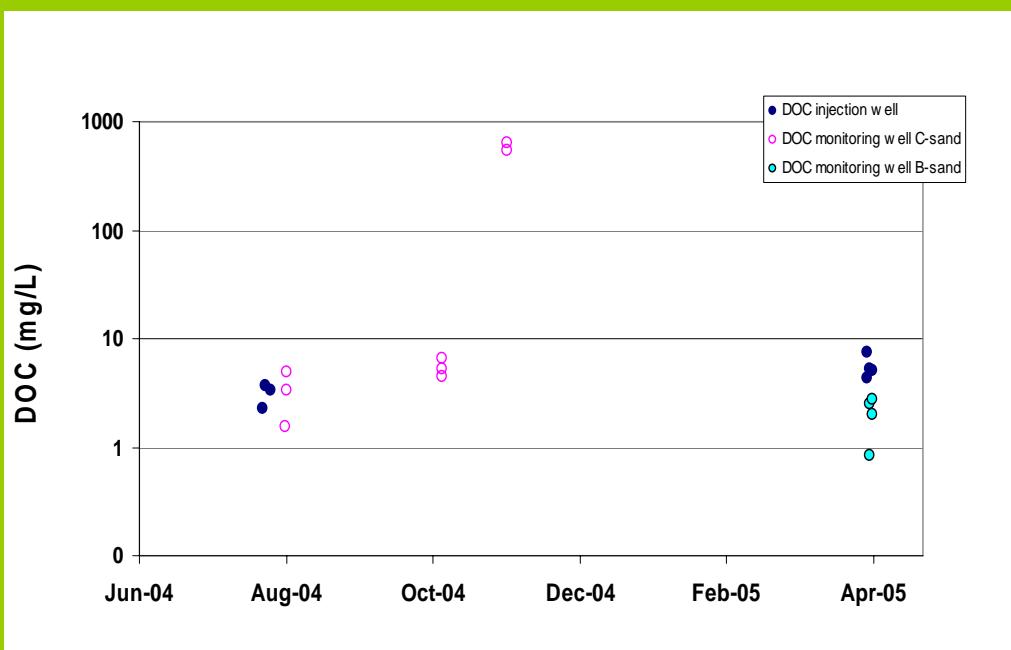


Fe, Mn, Zn conc. in Frio samples (10/5/04-10/7/04)



Organics in Produced Water

(mg/L)



ACETATE & ACID ANIONS	10,000
BTEX	60
PAHs	10
PHENOL	20
4 – METHYL PHENOL	2
BENZOIC ACID	5
4 – METHYL BENZOIC ACID	4
2 – HYDROXY BENZOIC ACID	0.2

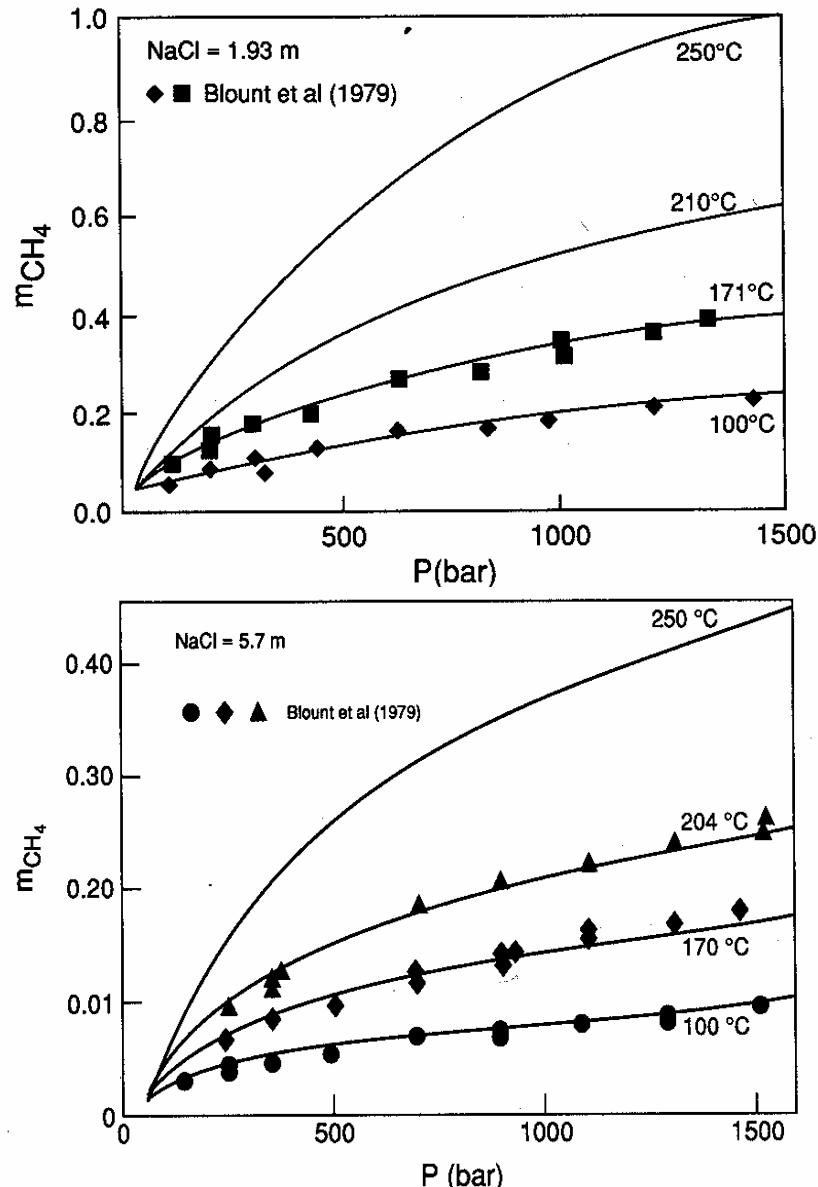
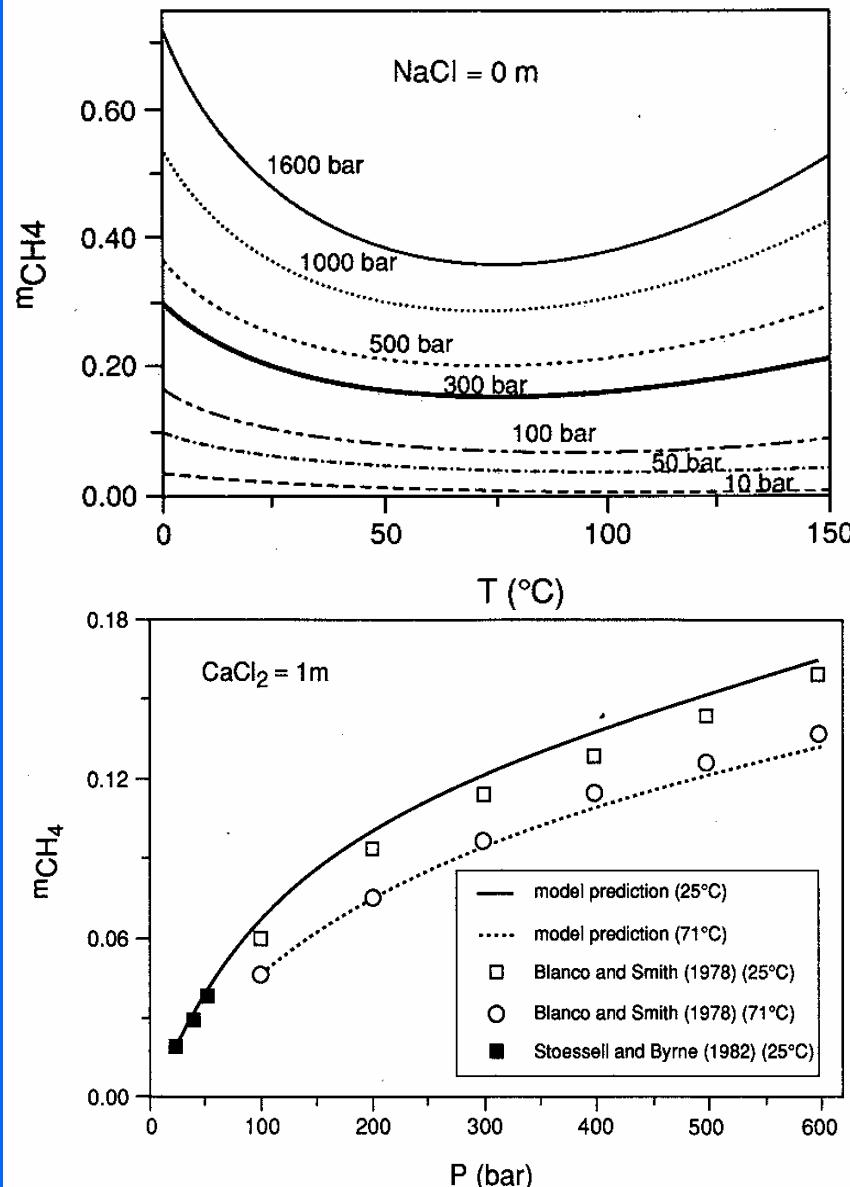
Chemical Composition of Frio Gases

**Frio formation water at saturation with CH₄

	Injection well before CO ₂ injection 04FCO2-102	Monitoring well before CO ₂ injection 10-7-04 @ 2:15 am	Monitoring well after CO ₂ injection 10-13-04 @ 20:37	Monitoring well "B" sand 05FCO2-110
He	0.0077	0.0026	0	0.0124
H ₂	0.0401	1.36	0.191	0.285
Ar	0.0418	0.0207	0	0.0608
O ₂	0.0719	0	0	0.748
CO ₂	0.31	0.0040	96.8	0.208
N ₂	4.15	3.60	0.037	5.17
CO	0	0	0	<0.001
CH ₄	93.4	94.8	2.94	93.4
C ₂ H ₆	0.149	0.161	0.0052	0.103
C ₃ H ₈	0.0086	0.0021	0	0.0012
C ₄ H ₁₀ +	1.76	0.0037	0	<0.0005

volume%, normalized

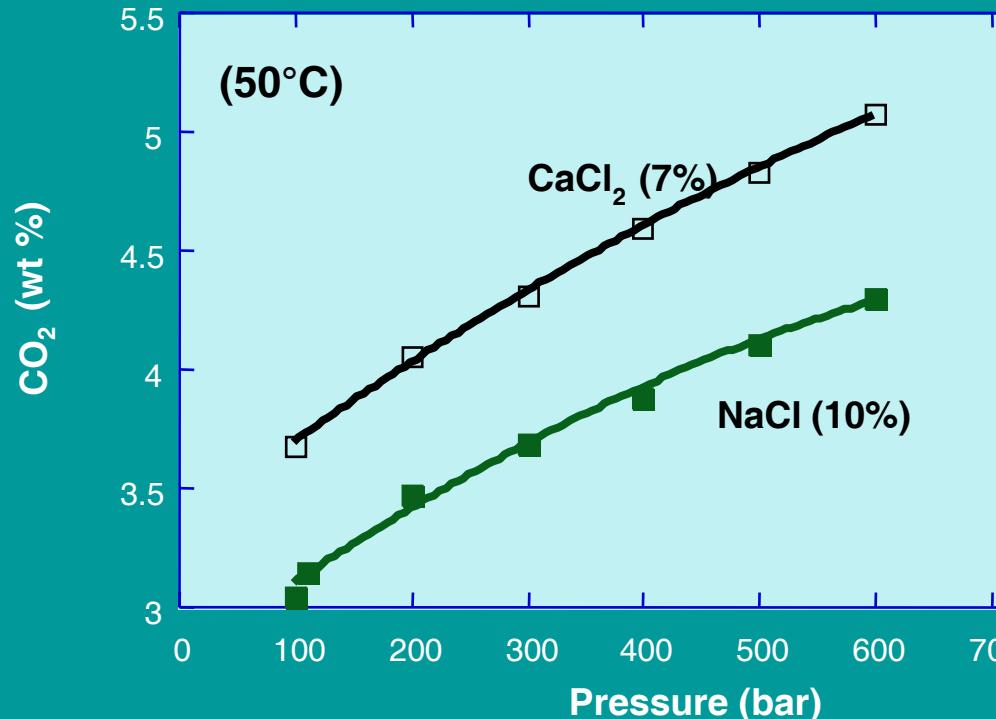
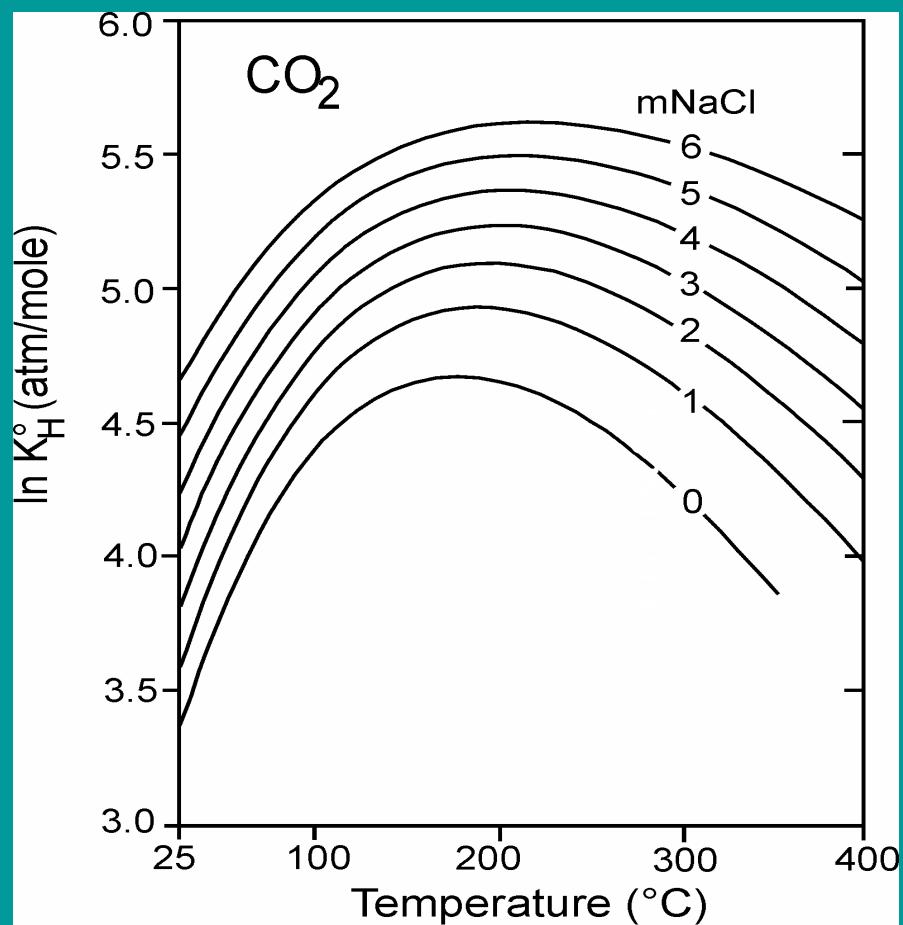
Solubility of CH_4 in Aqueous Solutions



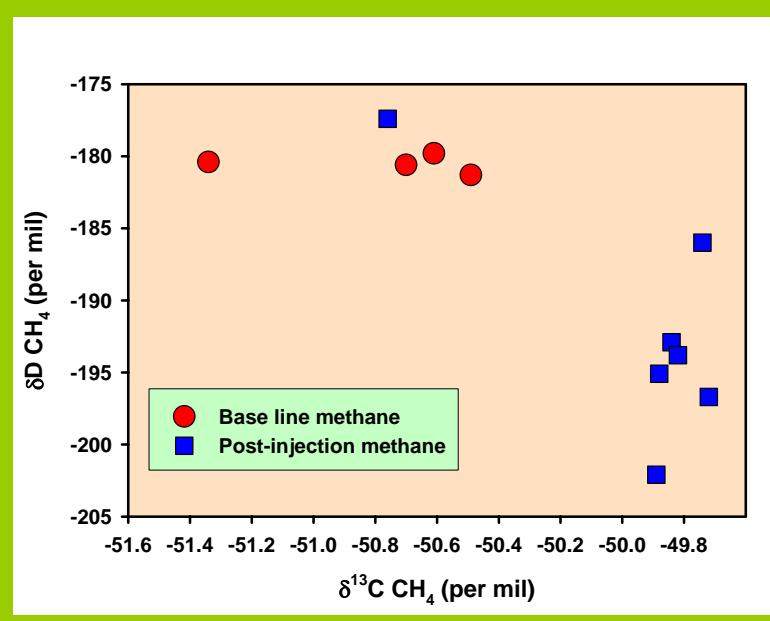
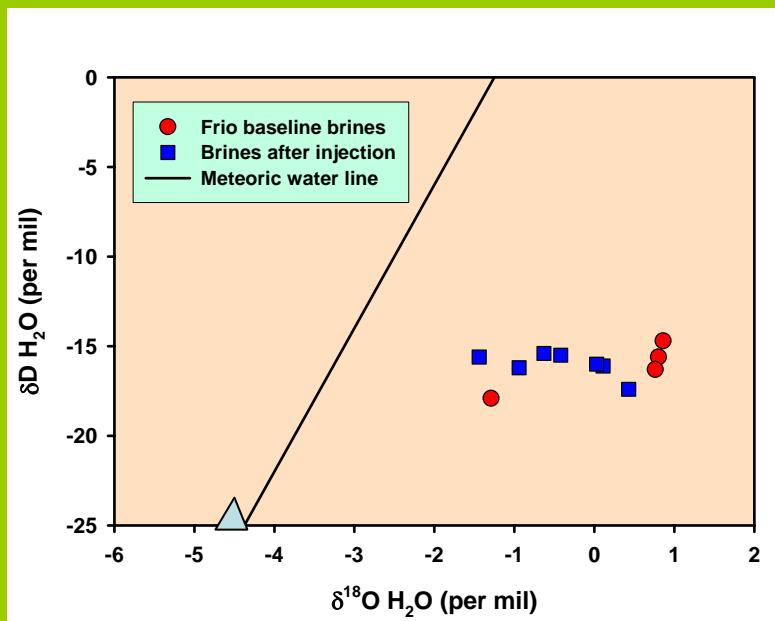
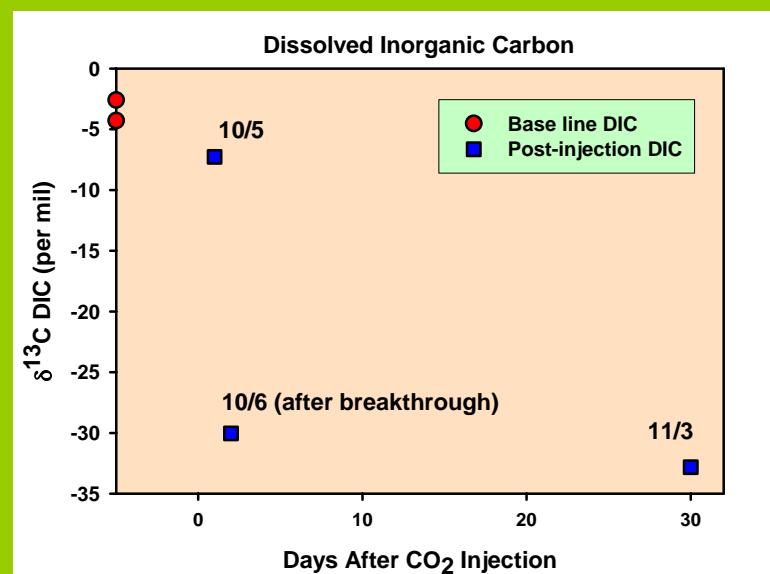
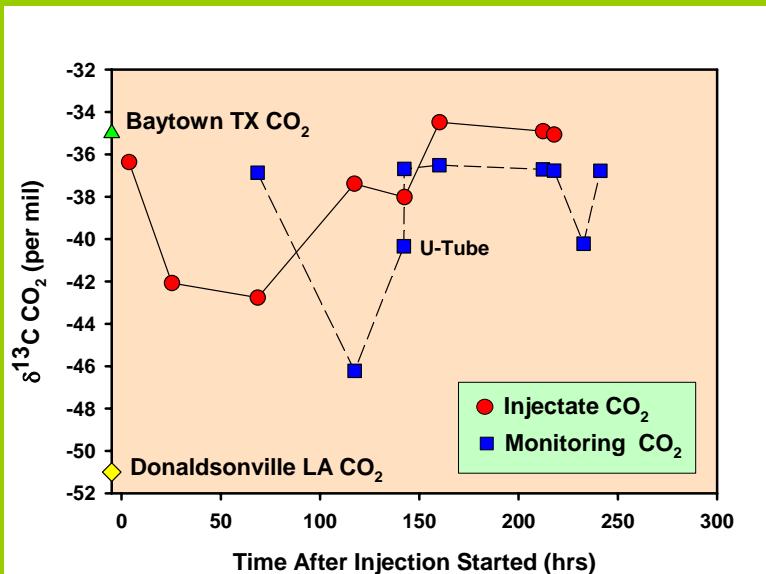
Duan et al., 1992

Solubility of CO₂ in water as f (t, P & chemical composition)

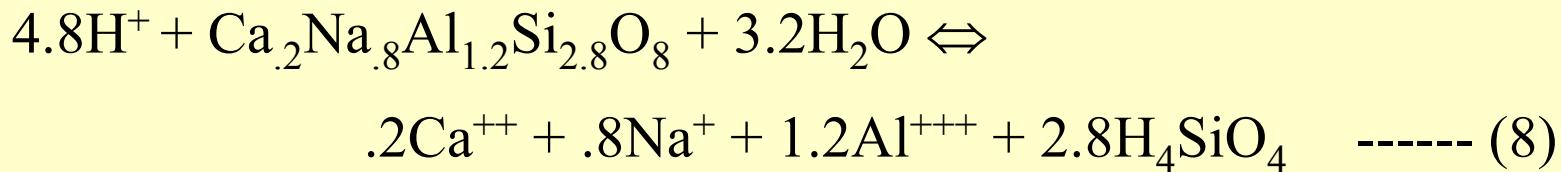
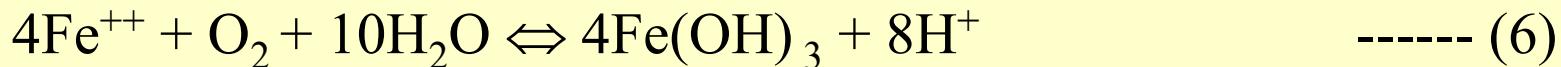
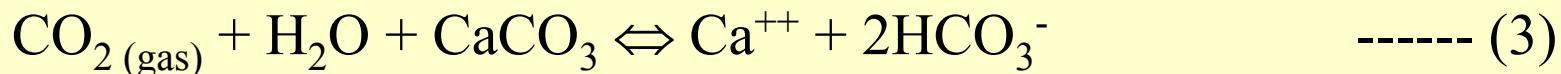
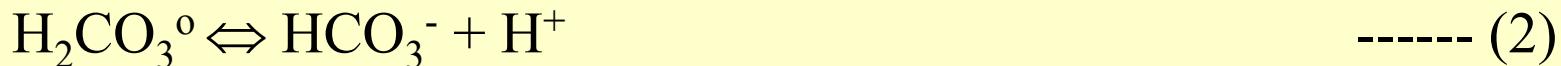
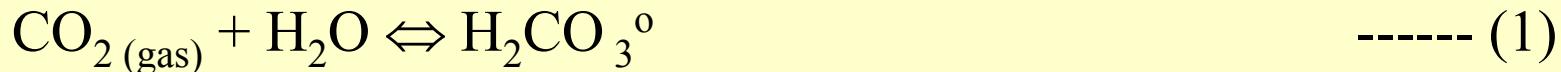
Drummond (1981); Rosenbauer et al., 2003

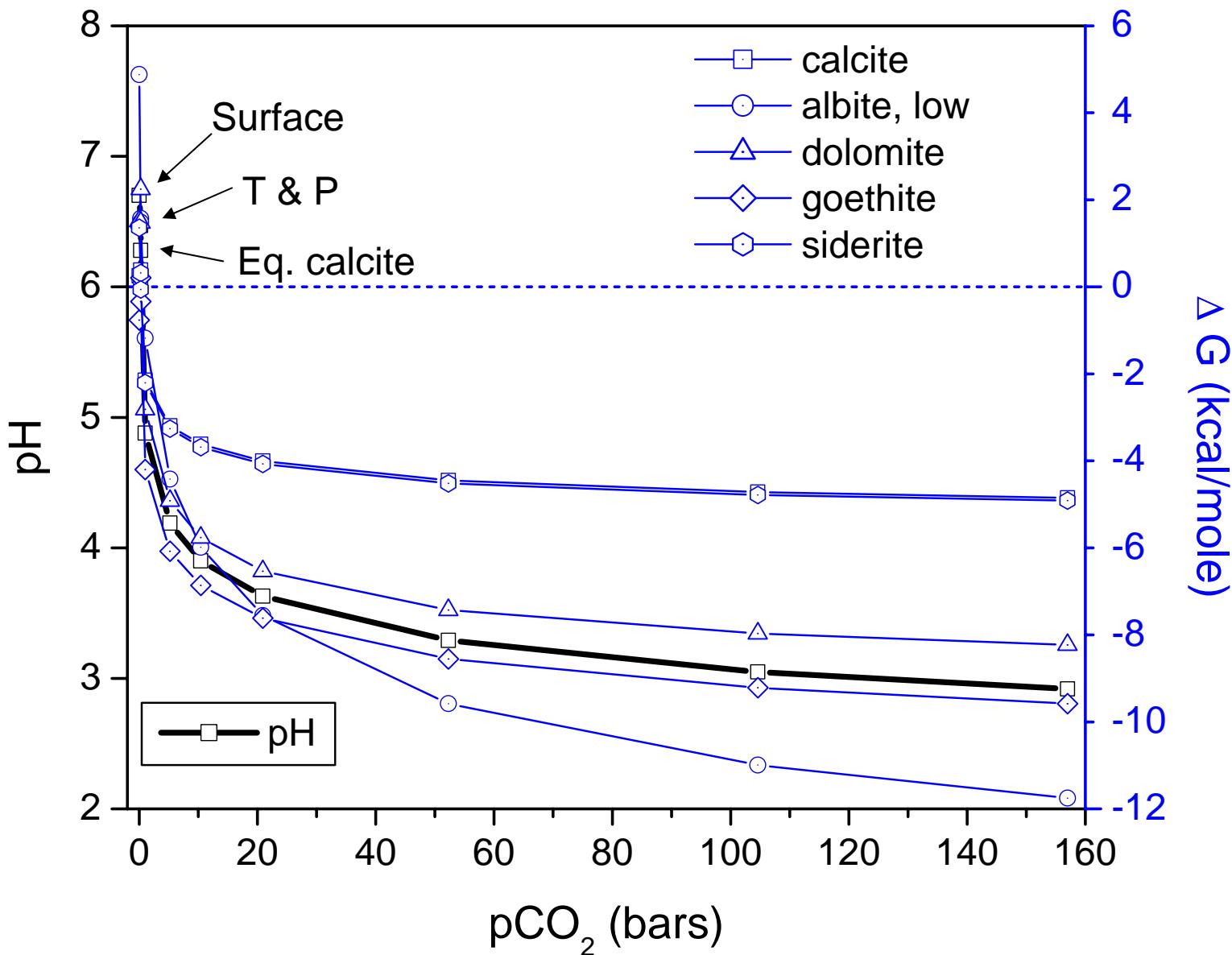


Isotope data- CO₂, H₂O, CH₄ & DIC



Important Mineral-Water-Gas Interactions in Frio

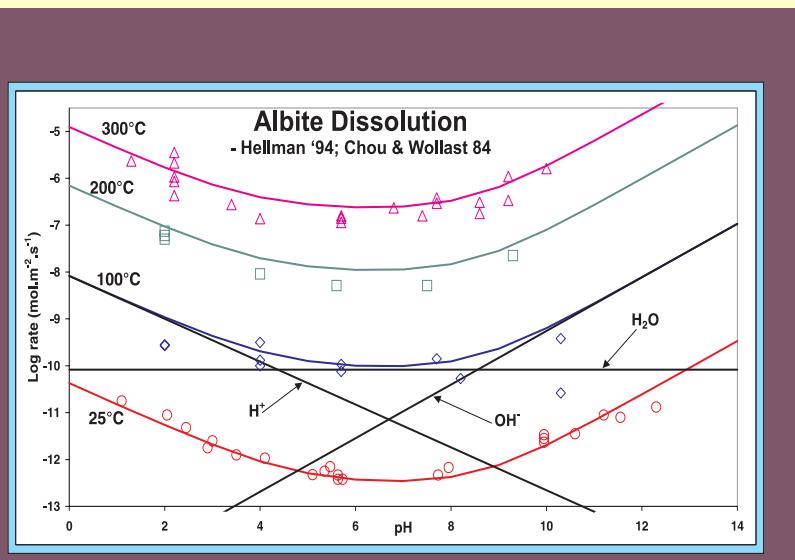




CO₂ Sequestration: Geochemical modeling

(Palandri, Kharaka, 2004)

$$\frac{dm}{dt} = - SA \sum_i [A_i e^{-E_i/RT} \prod_j a_{i,j}^{n_{i,j}} f_i(\Delta G_r)]$$



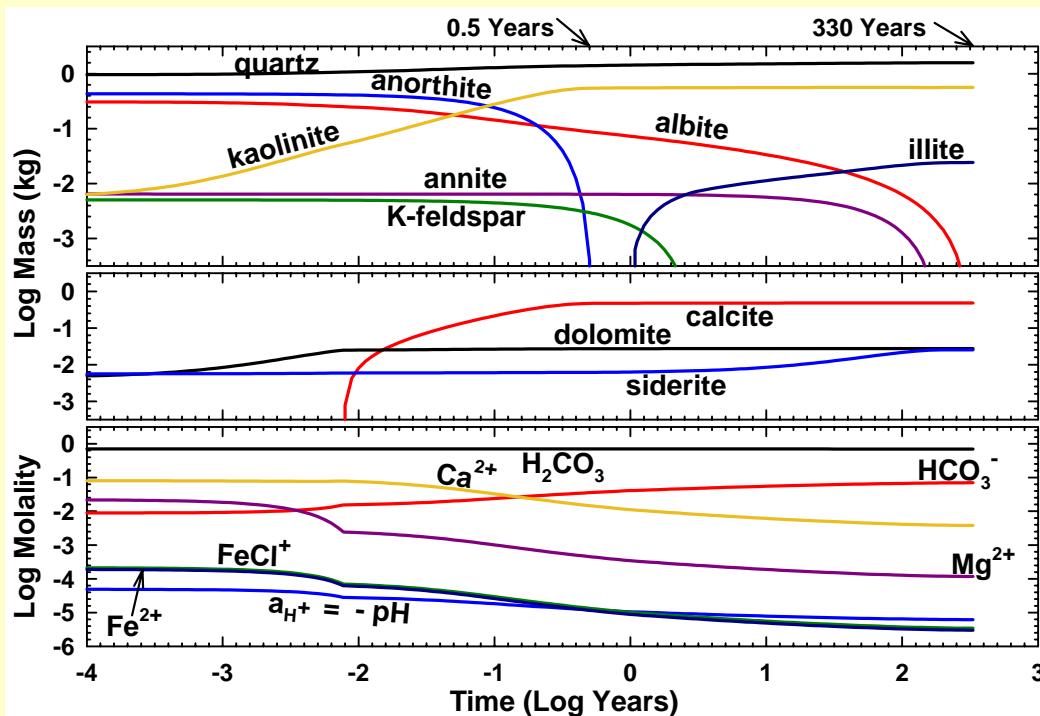
USGS

Selected rates in D.I. Water at 25°C (log.moles.m⁻².s⁻¹)

-5.81	*calcite	-10.78	magnetite
-7.00	*dawsonite	-12.04	albite
-7.32	hematite	-12.41	K-feld
-7.52	pyrite	-12.55	biotite
-7.53	*dolomite, sed	-12.72	enstatite
-8.60	*dolomite, hydroth	-13.18	kaolinite
-9.12	anorthite	-13.34	quartz
-9.34	*magnesite	-13.55	muscovite, illite
-9.79	chrysotile		
-10.64	forsterite/fayalite		

Compilation of a database of rate parameters for mineral dissolution and precipitation for use in prediction of rates of water/ rock/gas interaction

Example: CO₂ sequestration in Ca-bearing arkose



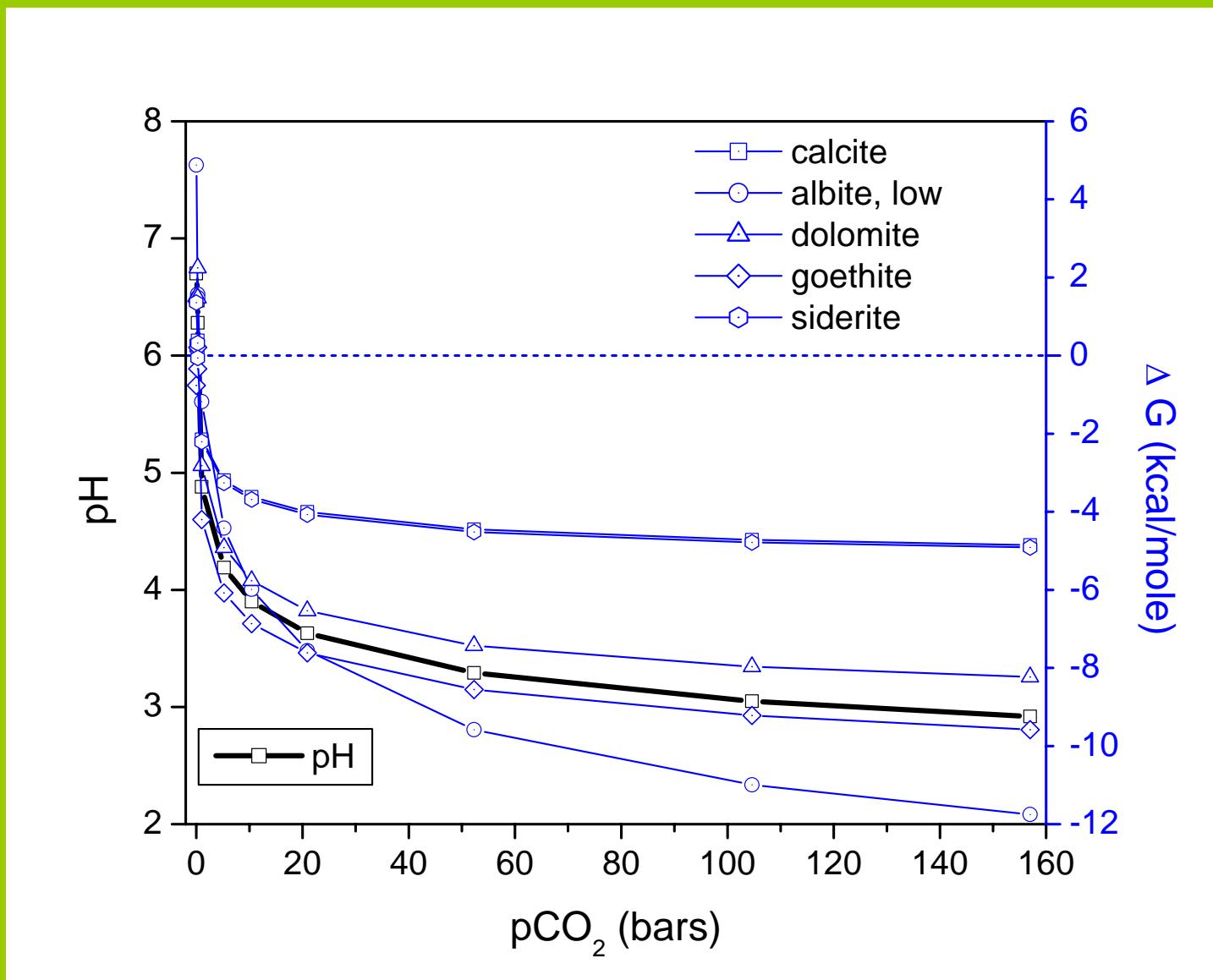
Summary and Conclusions

- 1- The Frio brine is saturated with CH₄ has a salinity of ~93,000 mg/L TDS, and is a Na-Ca-Cl type water; composition of formation water that determines CO₂ interactions in sedimentary basins is highly variable—TDS=2,000-460,000 mg/L.
- 2- Though useful parameters may be obtained from electrical logs and the National Geochemical Database, careful sampling & analysis of brine samples are necessary to study interactions.
- 3- Field determinations of alkalinity, pH and gas compositions are excellent and rapid methods for tracking the injected CO₂.
- 4- The low pH values resulting from CO₂ injection could have important environmental implications:
 - a)-Dissolution of minerals, esp. iron oxyhydroxides could mobilize toxic components;
 - b) dissolution of minerals may create pathways for CO₂ and brine leakage.
- 5- Where residual oil and other organics are present, CO₂ may mobilize organic compounds; some may be toxic.

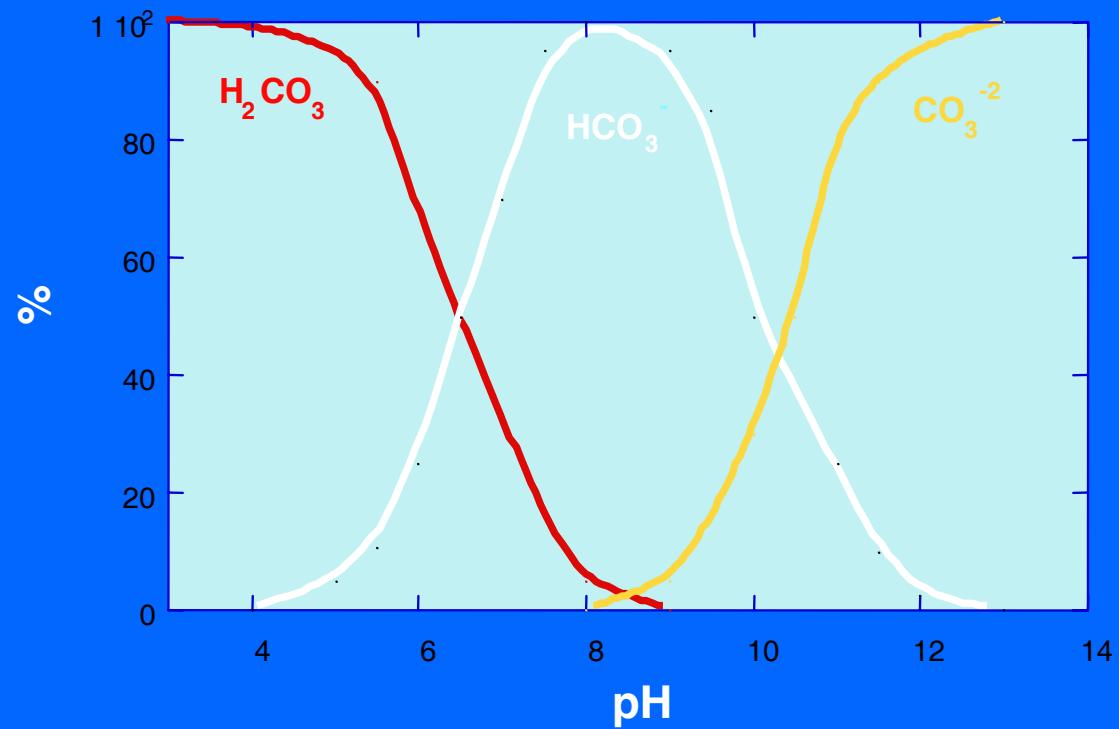




Computed pH and saturated states of selected minerals at T & P



Idealized carbonate speciation



KINETICS OF MINERAL DISSOLUTION AND PRECIPITATION

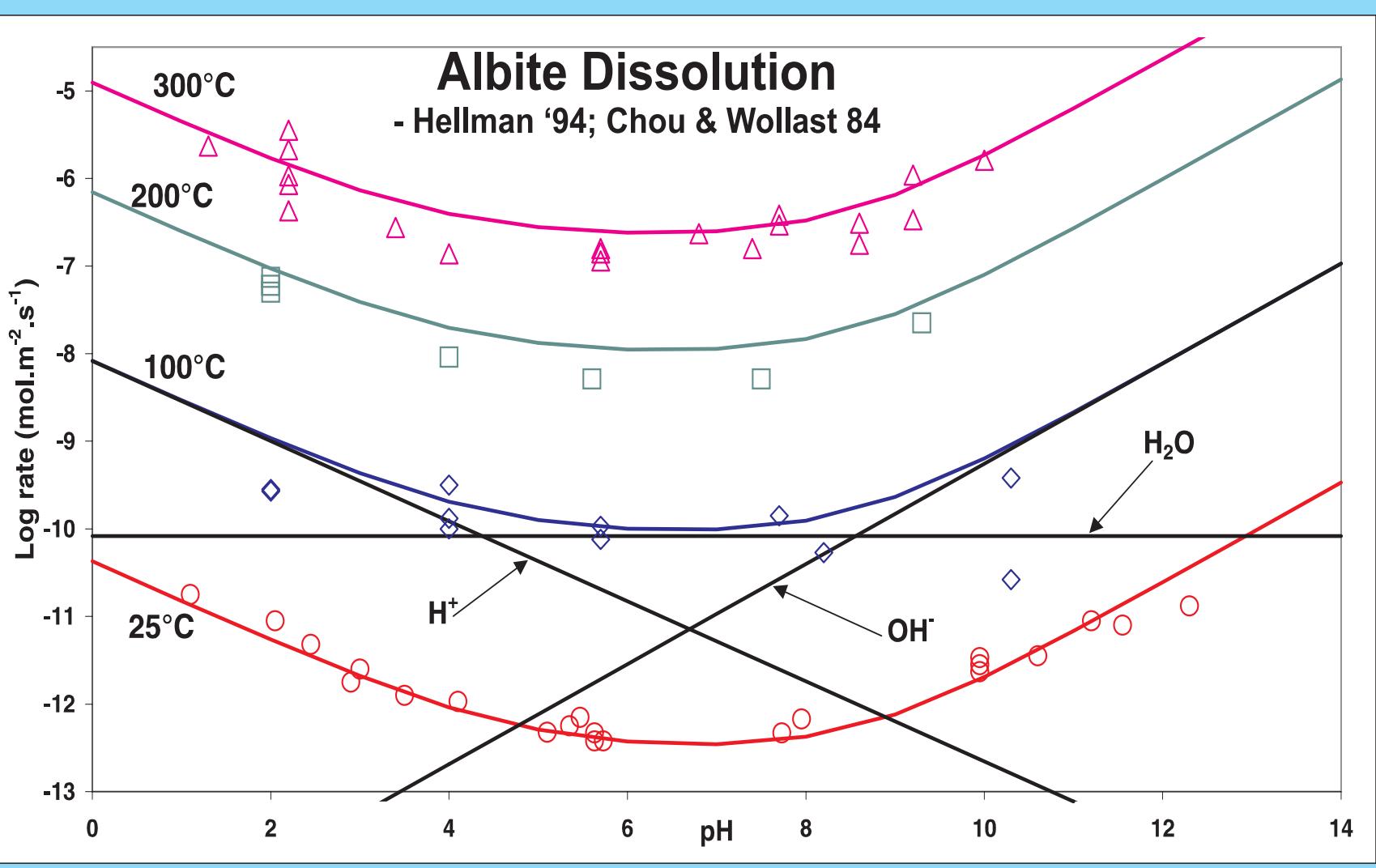
$$\frac{dm}{dt} = -SA \sum_i [A_i e^{-E_i/RT} \prod_j a_{i,j}^{n_{i,j}} f_i(\Delta G_r)]$$

The surface area is SA (m^2), A is the Arrhenius pre-exponential factor ($\text{mol m}^{-2} \text{ s}^{-1}$), E is the activation energy (J mol^{-1}), T is the temperature (K), R is the gas constant, $a_{i,j}$ is the activity of the j^{th} species in the i^{th} reaction mechanism, and $n_{i,j}$ is the reaction order. The term $f(\Delta G_r)$ is a dimensionless function of the chemical affinity to account for slowing of reactions as equilibrium is approached:

$$f(\Delta G_r) = (1 - \Omega^{p_i})^{q_i} = \left(1 - \left[\frac{Q}{K}\right]^{p_i}\right)^{q_i}$$

Omega ($\Omega = Q/K$) is the mineral saturation index where Q is the activity product, and K is the equilibrium constant. The parameters p_i and q_i are empirical and dimensionless, although p_i can be predicted from transition state theory.

$$\frac{dm}{dt} = SA \left[k_{acid}^{25^\circ C} e^{\frac{-E_{acid}}{R(T-298.15)}} a_{H^+}^{n_{1a}} a_{Fe^{3+}}^{n_{1b}} (1 - \Omega^{p_1})^{q_1} + k_{neut}^{25^\circ C} e^{\frac{-E_{neut}}{R(T-298.15)}} (1 - \Omega^{p_2})^{q_2} \right. \\ \left. + k_{base}^{25^\circ C} e^{\frac{-E_{base}}{R(T-298.15)}} a_{H^+}^{n_3} (1 - \Omega^{p_3})^{q_3} + k_{HCO_3^-}^{25^\circ C} e^{\frac{-E_{base}}{R(T-298.15)}} a_{HCO_3^-}^{n_4} (1 - \Omega^{p_4})^{q_4} \right]$$

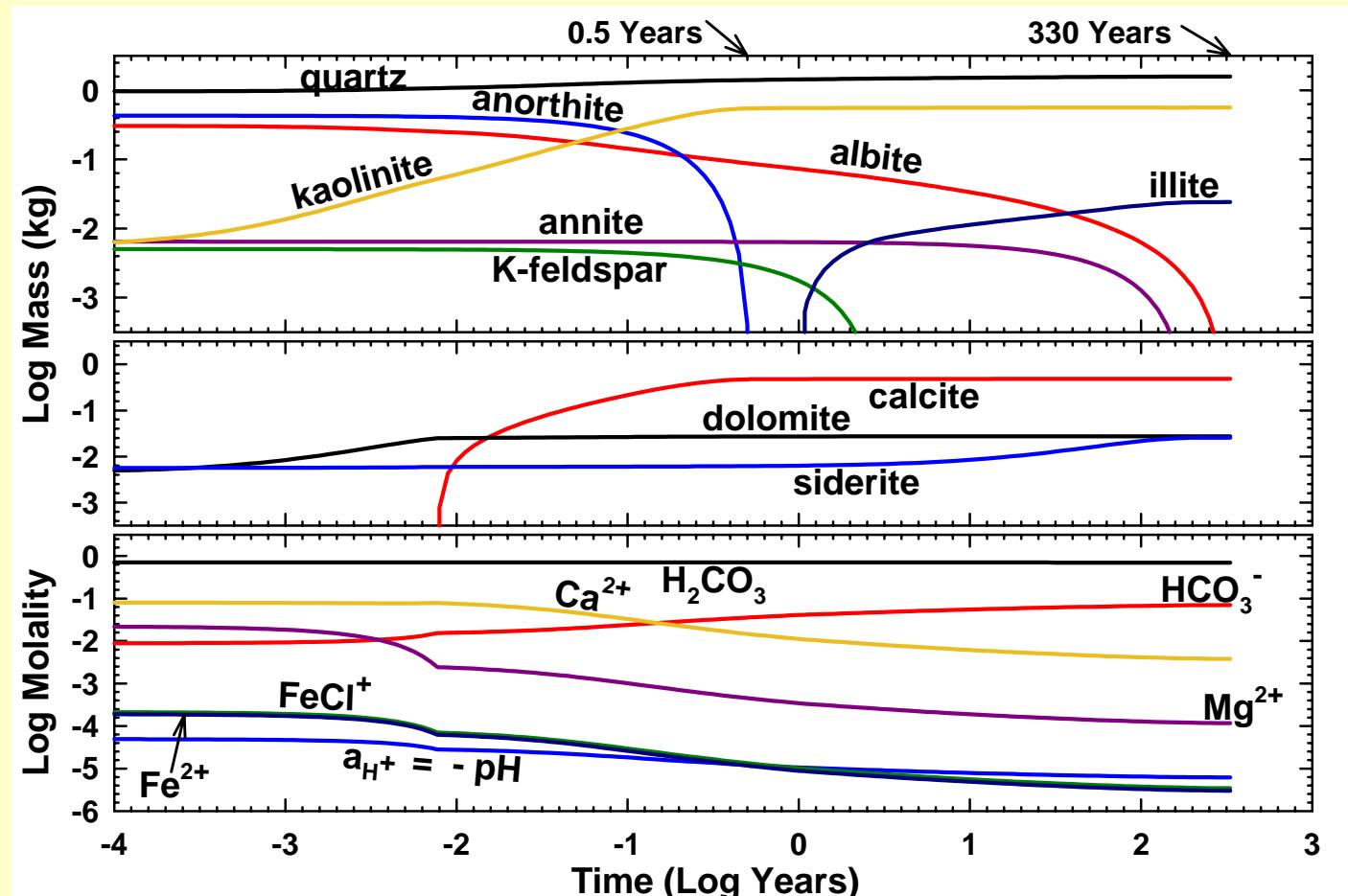


CO_2 Sequestration: Theoretical studies

(Palandri, Kharaka, 2004)

Compilation of a database of rate parameters for mineral dissolution and precipitation for use in geochemical modeling: Prediction of rates of water/ rock/gas interaction

Example simulation: CO_2 sequestration in Ca-bearing arkose



Fe, Mn, Zn conc. in Frio samples (6/04-11/04)

